An Alternative for the End-of-life Phase of Flame Retardant Textile Products: Degradation of Flame Retardant and Preliminary Settings of Energy Valorization by Gasification

Sohail Yasin,[a,b,c,d,]* Massimo Curti,[b] Giorgio Rovero,[b] Nemeshwaree Behary,[c,d] Anne Perwuelz,[c,d] Stephane Giraud,[c,d] Gianluca Migliavacca,[b] Guoqiang Chen,[a] and Jinping Guan [a,]*

It is well established that current flame retardant (FR) products at disposal generate various ecological hazards. Irrespective of their environmental impacts, the FR market is growing and is estimated to reach 2.8 million tons globally in 2018. In the textile domain, FRs are incorporated into baby clothing, pushchairs, car seats, *etc*. When disposed, these FR textile products end up in a landfill or are incinerated. These disposal processes are unsustainable. With landfilling, there is a huge chance of the FR product leaching into the environment. Similarly, FRs decrease energetic yields in the incineration process due to incomplete combustion. To cope with such issues, degradation and elimination of the FR product from the textile products before disposal could be a sustainable alternative. This study dealt with the preliminary degradation of flame retardant from the cotton textiles and its thermal characterization. Energy valorization by gasification is considered beneficial opposed to incineration with overall low energy recovery. The initial optimum gasification conditions including FR-treated cotton as a feeding material and potential outcomes of FR-treated cotton after degradation were characterized.

INTRODUCTION

Flame retardants (FRs) are extensively used for industrial and household applications. They are found in firefighter clothing, paints, furniture, baby clothing, pushchairs, car seats, *etc*. The global consumption of FRs is rapidly increasing. In 2006, the consumption of FRs in Europe was estimated at 465,000 tons (EFRA 2007) and will reach 2.8 million tons globally in 2018 (Freedonia 2013; ICL 2015). The textile industry actively utilizes FRs, depending on the application. These FRs include semi, non-durable, and durable finished textiles, where the durability is dependent on the binders. The durable/permanent FR textiles are used in high-performance applications (Birnbaum and Staskal 2004), while the non- and semi-durable FRs are used in the domestic sector, in products such as disposable medical gowns, curtains, carpets, and beddings. However, adverse environmental impacts of FRs in their production, consumption, and disposal phases can be found (Hansen and Lent 2007). The use of different chemicals to bring

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special fire safety and healthcare attributes to the textile products has shown links to severe health effects from asthma to cancer (Hansen and Lent 2007). Comparatively, to fulfill the safety regulations to avoid fire incidents, FRs are used in various indoor and outdoor products *i.e.*, electrical/electronic appliances, transport vehicles, furnishings, and upholstery products (EFRA 2013; Mizouchi *et al.* 2015). In addition, FR products have been found in the air (Saito *et al.* 2007), dust (Stapleton *et al.* 2009), surfaces, drinking water (Bacaloni *et al.* 2007; Rodil *et al.* 2012), and wastewater (Meyer and Bester 2004). Flame retardants have also been found in some fish species (Kim *et al.* 1986; Sundkvist *et al.* 2010) and in human breast milk (Kim *et al.* 1986). Moreover, prohibiting or replacing the FR product is rather a difficult task, which involves various requirements of regulation to achieve the necessary fire safety levels to pass the fire test standards (Lavoie *et al.* 2010; Yasin *et al.* 2016c).

Apart from their presence in daily life, recycling, landfilling, or even incineration as a disposal option for different flame retardant products can lead to certain environmental pressures and difficulties. For instance, recycling of certain flame retardant products can contaminate the waste stream, while landfilling can lead to chemical leaching into the soil and potentially contaminate the food supply, and incineration of those flame retardant products can create dioxins and furans (Shaw *et al.* 2010). Besides, surroundings of the disposal sites such as recycling, landfilling, and incineration facilities have been found to have high concentrations of flame retardants (United Nations Report 2010).

Presently, information on the exposure of FRs in textile products to environmental pathways is scarce, especially at the end-of-life phase. At disposal, the FR textile products end up in landfills or in incinerators. It is well-known that the discarded FR textile products pose potential concerns of leaching through the soil, as the rainfall permeates the ground and degrades the surface and ground water (Wargo *et al.* 2013), including the toxic emissions from the incomplete combustion of FR products in the incinerators (Simonson *et al.* 2000). There is currently no specific treatment for FR textile products prior to disposal, to avoid toxic emissions during the incineration process and leaching of chemicals in a landfill (Nazaré 2009). Moreover, human toxicity linked to the improper treatment of FR products is mainly during the incomplete incineration (Jonkers *et al.* 2016).

The energy recovery from the FR-treated cotton textiles is hurdled due to low energy yield and possible toxic emissions during the combustion of FR textile products. As an alternative, the degradation and elimination of FR substances from textile products prior to their disposal can overcome such challenges. Moreover, the FR-treated cotton products waste has chemical potential, as it can be changed into medium heating value syngas from gasification. The gas consists of the essential components for the production of fuel and chemical intermediates, such as hydrogen, methane, and carbon monoxide.

In the author's previous study (Yasin *et al.* 2016a), the degradation of durable FR product from the cellulosic fabric, with an advanced oxidation process (AOP), was demonstrated. Thus, the flame retardant textile products can be reused for alternative energy valorization, instead of being incinerated or disposed of into a landfill. The AOPs, such as Fenton's reaction, are well-known for their capability to degrade and mineralize a wide range of organic compounds that are sometimes resistant to conventional biological oxidation. The degradation of FR product from the cotton fabrics will possibly increase the combustion properties of the FR cotton fabrics compared to non-degraded ones. This study employs the same Fenton's reaction to the FR textiles prior to the gasification process.

EXPERIMENTAL

Materials

FR treatment for the cotton fabric

Cotton fabric specimens were cut into 18 cm x 18 cm squares to be treated with Pyrovatex CP new (Huntsman, Woodlands, USA), which includes an active organophosphorus FR ingredient named N-methylol dimethyl phosphonopropionamide (MDPA). The sampled cotton fabrics were dyed and plain woven with 170 g per square meter (GMS). The FR finish solution was prepared according to the formulation instructions given on the supplier's (Huntsman, Woodlands, USA) data sheet. The FR treatment on the fabric was done with a pad-dry-cure process, performed with a conventional process that included keeping the drying and curing temperatures at 100 °C and 150 °C for 4 min to 5 min in a curing oven. A gap of 5 min between drying and curing was given, which allowed the fabric to cool down a little, since continuous drying and curing would degrade the fabric. Care should be taken while curing because the acidic nature of the FR solution may degrade the fabric if the specified curing time is exceeded.

After curing, the samples were neutralized with an alkaline bath for at least 2 min. Neutralization was performed by dipping the samples in a solution of sodium carbonate (Na_2CO_3) 30 g/L and water. The cotton fabric samples were then washed thoroughly with water after neutralization, and then oven-dried at 100 °C until the samples were completely dried. Analytical grade chemicals (Carlo-Erba, Milan, Italy) and distilled-deionized water were used in the solution preparations.

Degradation of FR product from the fabric

The degradation of the FR product from the cotton fabric was performed with reference to the author's previous study (Yasin *et al.* 2016a). In this study, three different concentrations of Fenton's reagents were used to degrade and eliminate the FR product from the cotton fabric. The Fenton's reagents used had a ferrous source ($FeSO_4.7H_2O$) of 100 mg/L, 200 mg/L, and 500 mg/L, and a constant quantity of 2 g/L of a hydrogen peroxide catalyst (H_2O_2, 98% in aqueous solution).

The reaction solutions were prepared using iron sulfate, hydrogen peroxide, and distilled water, with a final volume of 1 L for each reaction. The flask was covered with aluminum foil to prevent any light from entering the Fenton's reaction. A single cotton fabric sample was then submerged in each prepared reaction solution and kept at room temperature for 1 h. Because Fenton's reactions are highly sensitive, the glassware was washed with detergent and rinsed properly to avoid any interference in the reaction. The pH of the reaction solution was adjusted to 4 using a 1 M solution NaOH or a 1 M solution H_2SO_4, followed by the addition of the requisite quantity of H_2O_2 and $FeSO_4.7H_2O$.

To quench the Fenton's reaction, a solution was prepared with 40 g/L of NaOH and water (Pontes *et al.* 2010). The three fabric samples that were kept in the Fenton's reaction solution were transferred into a flask containing one liter of 40 g/L NaOH solution for 20 min. After quenching, the samples were washed thoroughly with water and oven-dried at 100 °C until the fabric samples were completely dried.

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Methods

Degradation and removal characterization of FR product

Fourier transform infrared spectroscopy (FTIR) was performed with a Thermo Nicolet 5700 FTIR spectrometer (ThermoFisher, Waltham, USA) within the wavenumber range 4000 cm^{-1} to 600 cm^{-1}.

The composition of FR-treated cotton before and after the degradation were analyzed with the help of energy-dispersive X-ray spectroscopy (EDS) that was performed using a ZEISS Supra 40 FESEM (Carl Zeiss, Oberkochen, Germany) equipped with an Oxford INCA energy-dispersive X-ray detector (Oxford Instruments plc, Abingdon, UK) (Si (Li)) with a resolution of 133 eV at (MnKα).

The thermogravimetric analysis (TGA) was performed using a Thermogravimetric Analyzer TGA 2950, (TA Instruments, New Castle, USA). The TGA was conducted in air, where the samples were heated from 20 °C to 800 °C at a constant heating rate of 10 °C/min.

The differential scanning calorimetry (DSC) was carried out (SDT 2960 DSC-TGA model, TA Instruments, New Castle, USA) with samples weighing between 1 mg and 5 mg, and measured from 40 °C to 800 °C nitrogen/air flux was 100 ml/min, increase rate of temperature was of 10 °C/min.

Gasification parameters and pellet preparation

During the gasification process, a material (normally a biomass) is burned in the presence of controlled oxygen, which yields synthetic gases as gaseous fuel. The gas is processed to make different chemical products or biodiesel. Consequently, gasification is a major environmental approach to attain biomass energy. The gasification process is dependent on certain operating parameters including gasification temperature, flow rates, oxidizing agents, feed type, properties, and design of the gasifier (Kumar *et al.* 2009). Gasifiers are classified based on the types of bed and flow, while the gasifier beds are either a fixed-bed or a fluidized bed (Bernocco 2013). Spouted bed gasifiers are special cases of fluidization and have demonstrated various advantages. These advantages include relatively lower gas flow rates, the ability to handle coarser solid particles, and a hydraulic structure that prevents segregation (Massimo 2015).

A spouted bed pilot gasification unit (Politecnico di Torino, Turin, Italy) was utilized to produce and analyze the syngas; the unit is represented in Fig. 1. The gasification unit is based on a square spouted bed that is 200-mm thick. A preheated spouting gas was generated in a burner where water was sprayed into the combustion gas, liquefied petroleum gas (LPG), to reach a suitable steam concentration. Downstream of spouting, the gasification product was cleaned from the powders in a cyclone, followed by a water scrubber for cooling and absorbing the soluble acid components. The reacting pellets were prepared manually, off-line, and were stored in an upper bin, continuously metered, and introduced in the spouted bed reacting zone from the side openings. Nevertheless, various configurations, such as standard spouting and spouting with secondary fluidization, were considered with the insertion of a draft tube as an auxiliary fluidization. The auxiliary fluidization is expected to provide advantages for larger units in terms of reaction control (Massimo and Rovero 2015).
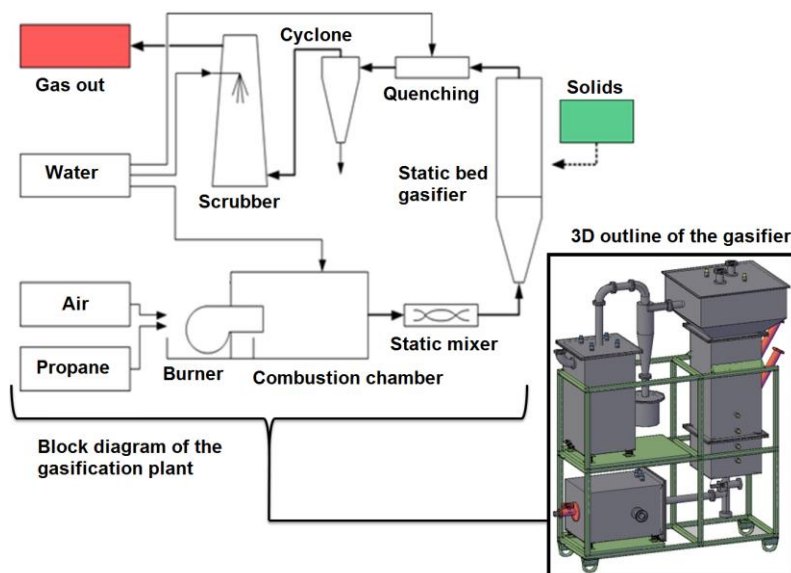
Fig. 1. Schematic illustration of the customized spouted bed gasifier

The spouted bed gasifier is used to improve the uniform distribution of feed particles; however, overfeeding will lead to plugging and reduce conversion efficiencies, and starve feeding will lead to a decrease in gas yield (Kumar *et al.* 2009; Massimo and Rovero 2015). Therefore, an optimum feed rate is required for an effective gasification system. Disposed textile waste is generally processed in bulk without any modifications, and it is ultimately incinerated. However, the fed particles size also plays an important role in the gasification outcomes, having larger surface areas per unit mass and larger pore sizes facilitate rapid heat transfer and gasification (Kirubakaran *et al.* 2009). In addition, smaller feed size resulted in more CH_4, CO, and C_2H_4 and less CO_2, leading to higher gas yields and gas energy content (Lv *et al.* 2004).

Industrial incineration plants utilize textile waste on a feed-as-received basis. By contrast, for pellet gasification, depending on the gasifiers, pellets with different particle sizes can be prepared at industrial scale with equipment capable of producing large quantities of particles from industrial textile waste. However, for the custom-designed gasification plant in this work, pellets of FR-treated cotton fabric were prepared to find the optimum conditions for the gasification. The following steps were taken to produce the textile pellets. The starch solution was prepared by adding 10 g to 15 g of sizing agent (maize starch) into 1 L of water, and it was used on the cotton fabric to create pellets. A solution of water and starch was heated at 120 °C with continuous stirring until the sizing solution went from translucent to clear and the consistency became thick. The starch solution was left to cool at room temperature.

The fabric samples were dipped in the sizing solution and then gently pressed and rolled to squeeze out the excess size solution from the fabric (Fig. 2B). The fabric rolls were then oven-dried for 30 min at 60 °C. The dried cotton fabric rolls were cut into 1-cm segments, a suitable size to be fed into a customized gasifier. The prepared fabric pellets (Fig. 2C) were used for the gasification in the pilot-scale equipment.
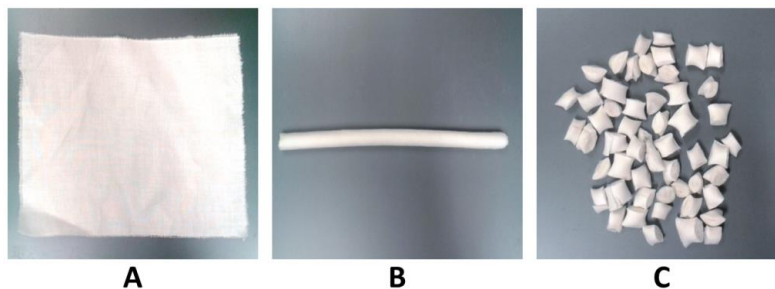
Fig. 2. Prepared cotton fabric pellets to be fed into the gasifier; A) plain cotton fabric, B) dipped in starched and rolled fabric, and C) cotton fabric cut into pellets

Preliminary tests and thermal transitory analysis

In gasification, all transitory thermal analysis requires a primary temperature, time duration, and important parameters (feed type, feeding rate, surface reaction of feed, *etc.*) for the quality and composition of the produced gas during gasification. Even though no thermal reactions were performed inside the reactor, to moderate the start-up phase and reach an effective state for gasification, a temperature above 800 °C inside the reactor was necessary. Therefore, the variation of temperature distribution over time was analyzed to find a suitable temperature for gasification to produce syngas. A preliminary gasification state, with an optimum flow rate for the prepared pellets to reach a temperature above 800 °C inside the reactor, was also analyzed.

RESULTS AND DISCUSSION

The functional groups on the surface of the FR cotton fabric were analyzed before and after degradation from the Fenton's reaction, as it provides details on changes in the absorbance. The results gathered using Fourier transform infrared spectroscopy (FTIR) showed a difference between the cotton fabric samples before and after the FR treatment (Fig. 3). The major peaks of the cotton fabric are OH stretching, placed around 3300 cm^{-1}, CH stretching around 2800 cm^{-1}, CH_2 symmetric stretching near 1400 cm^{-1}, CH stretching placed around 1300 cm^{-1}, CO stretching around 1020 cm^{-1}, and a C−O−C non-symmetric bond placed around 1200 cm^{-1}.

The FR treatment showed new characteristic peaks in the cotton fabric, for instance, carbonyl bands, CH_3 asymmetric peaks, CH_2 symmetric stretching, and CH_2 rocking bands (Lam *et al.* 2011). The cotton sample treated with FR showed a visible C=O peak around 1660 cm^{-1}. This peak corresponded to the stretch of an amide group that was present in the FR agent instead of a possible absorbed water vibration. The vibration of phosphorus bonding (P=O) usually occurs around 1320 cm^{-1} to 1140 cm^{-1}, and is rather difficult to identify. There is often overlap of characteristic peaks and absorption of primary and secondary deformations in the OH group of cotton (Siriviriyanun *et al.* 2008; Lam *et al.* 2011). As aforementioned, it was difficult to identify the dominant FR groups, and similarly, there were no visible changes in the peaks after the Fenton's reaction. However, the FTIR of the FR-treated fabric that underwent the Fenton's reaction showed similar functional groups with possible O−O stretching and vibration at around 820 cm^{-1}, which indicates the presence of peroxides.
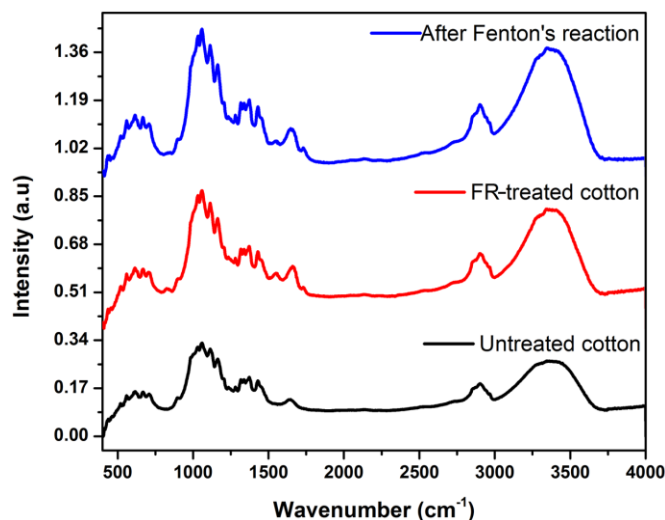
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Fig. 3. FTIR of cotton fabric and FR-treated fabrics before and after Fenton's reaction

The energy-dispersive X-ray spectroscopy (EDS) and scanning electron microscope (SEM) images of the cotton fabric samples are shown in Fig. 4. The EDS spectra analysis of the FR-treated cotton samples (Fig. 4A), shows the presence of phosphorus and traces of magnesium. The image also represents the presence of ferrous metal on the cotton fabric after the Fenton's reaction (Fig. 4B), along with traces of calcium.
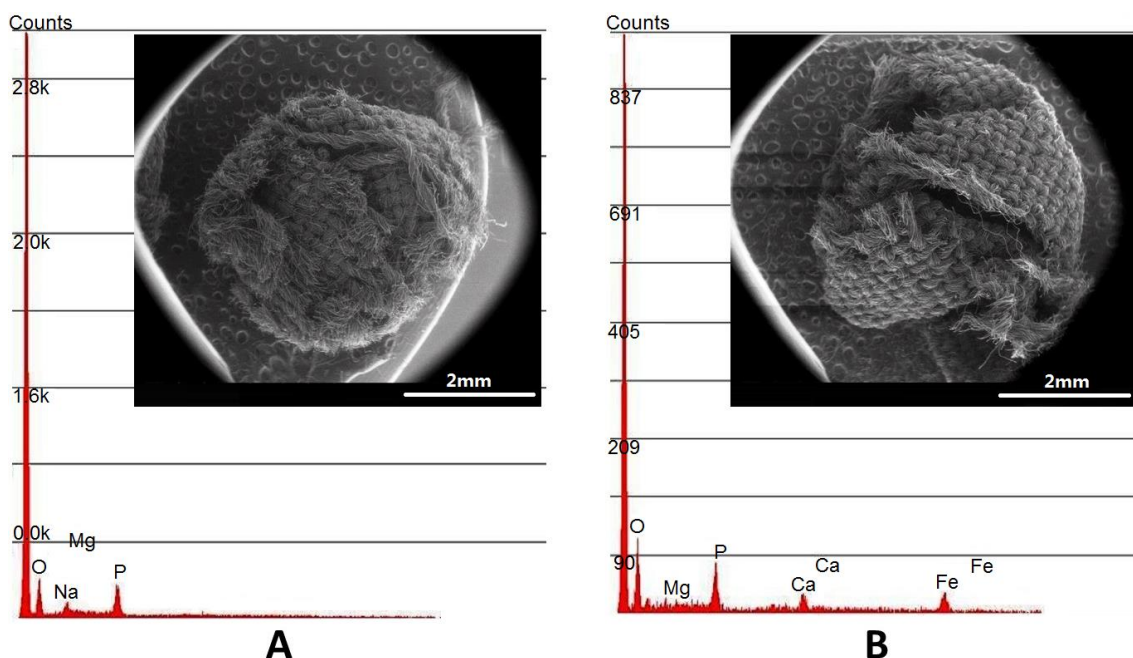

Fig. 4. EDS of cotton fabrics before (A) and after the Fenton's reaction (B), and the SEM image of the corresponding samples (inset)

Thermal gravimetric analysis (TGA) was performed in an open platinum sample pan, and the measurement was conducted in an aerobic atmosphere. The TGA technique was carried out in atmospheric air that was used for the thermal stability evaluation of the FR product. The samples weighing between 1 mg and 5 mg were placed in the sample pan,

and measured from 20 °C to 800 °C, at a heating rate of 10 °C/min, with continuous air flow. Figure 5 shows the TGA curves of cotton fabric without the FR treatment (control sample), FR-treated cotton, and FR-treated cotton fabric after Fenton's reaction with three different concentrations of ferrous salt. However, the highest concentration of the reagent ferrous source (500 mg/L) used was taken for further analysis.
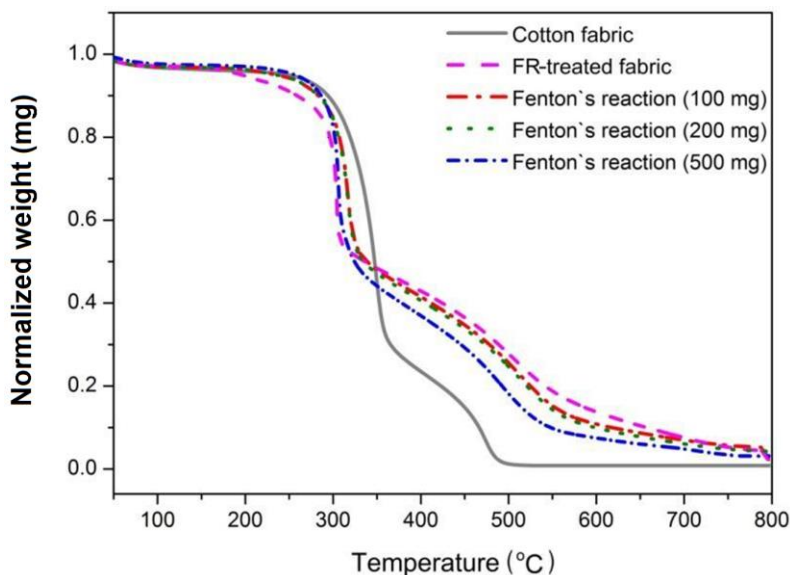

Fig. 5. TGA curves of the cotton fabric and the FR-treated fabrics before and after Fenton's reaction with varied concentrations of ferrous source
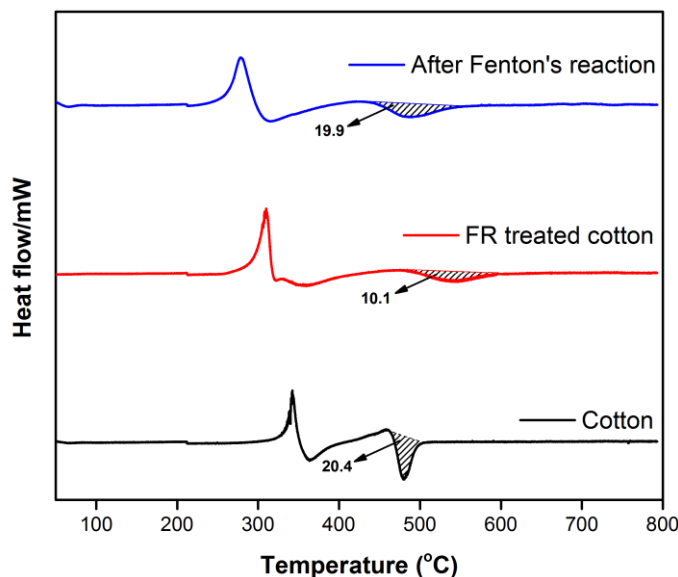

Fig. 6. Derivative DSC curves of cotton fabric and the FR-treated fabrics before and after Fenton's reaction. Attributional area: cotton = 20.4, FR-treated cotton = 10.1 and after Fenton's reaction = 19.9. Ratio of decomposition peak; (cotton: FR-treated cotton/1: 0.49), (cotton: after Fenton's reaction/1: 0.97)

A DSC in aerobic condition was carried out with samples weighing between 1 mg and 5 mg, and measured from 40 °C to 800 °C, at a heating rate of 10 °C/min. Suppression in the formation of flammable products can be seen in the DSC curves, as shown in Fig. 6.

Here, the shaded region represents the attributional area of the decomposition curve peaks. The ratio of decomposition was calculated for the comparative analysis.

General discussion

The durable FR product in this study was an organophosphorus compound, N-methylol dimethyl phosphonopropionamide (MDPA), it is one of the effective FRs used for cotton fabrics (Kalliala and Talvenmaa 2000; Ravichandrana *et al.* 2011). It withstands a great number of dry cleanings, launderings, or other cleaning procedures (Van der Veen and Boer 2012). In an effort to successfully degrade and eliminate the FR product from the cotton fabric, Fenton's oxidation reaction was employed. The Fenton's reaction is the simplest AOP technique; it can be utilized at adjacent pressures and temperatures. The Fenton's reaction utilizes two primary reagents, ferrous ion as the catalyst and hydrogen peroxide as the oxidant. The reaction of these reagents is mostly based on the generation of fleeting hydroxyl radicals (OH•) (Glaze *et al.* 1987), which are capable of oxidizing agents that react with the majority of organic compounds (Esplugas *et al.* 2002).

The FTIR curves in Fig. 3 show the presence of different functional groups in treated and untreated cotton fabrics. The SEM images show the plane structure of the fabric, but in the EDS images, the addition of an inorganic metal *i.e.,* ferrous, is visible after the Fenton's reaction. The presence of elements like magnesium (Mg) and calcium (Ca) was possibly due to the tap water used to wash the samples. Such impurities can be avoided by using distilled-deionized water for washing.

Extraneous elements shown through energy-dispersive electron spectroscopy (Fig. 4), like the inorganic ferrous compounds, could alter the required gasification outcomes, especially the quality of the syngas produced. However, ferrous compounds have the ability to catalyze the decomposition of ammonia at high temperatures. Ferrous compounds increase the ammonia content of gas at low temperatures by converting parts of tar and organic nitrogen to ammonia, if the gas contains a high tar load (Leppälahti *et al.* 1993). Moreover, ferrous compounds from the thermal residues are considered a recyclable material (ISWA 2006).

The thermal decomposition of the cotton fabric incorporated diverse stages. The first stage concerned the release of adsorbed water, which began at around 100 °C. The second stage was a fast weight reduction where decarboxylation and dehydration reactions delivered flammable gasses such as ketones, aldehydes, ethers, *etc*. The third stage began around 500 °C and related to the decomposition of char formed amid the second stage (Weiyi *et al.* 2011). The TGA curves in Fig. 5 show comparable three-stage combustion behavior between the cotton fabrics. The weight of the FR-treated cotton fabric at first decreased rapidly during decomposition temperatures, which enabled the FR-treated cotton to create a larger number of residues than the untreated cotton fabric. The MDPA FR finish works as a condensed-phase FR and helps char development (Egyed and Simon 1979). In this process the materials are subjected to a cut-off of air, which prevents heat transfer and lowers flammable gas emission to achieve the purpose of the FR additive. Moreover, the combustion starts at lower temperature to resist the flame's reaching high temperatures by creating a dense layer in the case of organophosphorus FRs. The phosphorus and nitrogen have a synergistic effect on the FR-treated cotton, expanding char development and producing the greatest amount of char at temperatures greater than 400 °C, while also generating high levels of aromatic volatiles such as toluenes, benzenes, and phenols (Horrocks 1996).

It is important to understand the chemical modification of the cotton fabric after the FR-treatment, which normally occurs in the amorphous regions of the cellulose. A cross-linker trimethylol melamine (TMM) is generally used for enhancing adhesive force of cellulosic material (Uddin 2013), this increase the nitrogen content for the synergistic effect of the FR-treatment with the phosphorus group of the MDPA (Yasin *et al.* 2016b). The cellulosic materials treated with FR having phosphorus and nitrogen elements, goes through catalyzed reactions of dewatering, decarboxylation and charring, which may produce other fragmented products (Zhu *et al.* 2004). Consequently, the influence of FR elements such as phosphorus and nitrogen in the cellulosic material can drop the gasification temperature drastically and increase or decrease the byproducts.

The lowest concentration of $FeSO_4.7H_2O$ (100 mg/L) utilized in this study showed a slight change in the thermal attributes of the sample of FR-treated cotton after Fenton's reaction. However, the highest concentration used (500 mg/L) showed a prominent change in the thermogravimetric properties of the fabric. Similarly, the char degradation found increased after 350 °C due to the possible effective kinetics of ferrous compounds from the Fenton's reaction. The FR-treated cotton showed a lower starting temperature of decomposition, which is due to the catalytically dehydration of the cellulose in the presence of organophosphorus flame retardant (Sandra *et al.* 2011). The decomposition temperature of the FR-treated cotton is lower than the untreated cotton and FR-treated cotton after Fenton's reaction.

The first derivative DSC curve of untreated cotton in Fig. 6 presents an endothermic/exothermic peak: the first is around 350 °C, which is usually linked with the formation of volatile products during cellulose decomposition and char crosslinking reactions (Langley *et al.* 1980). The second peak can be seen at about 480 °C, which presents an oxidation of previously formed volatile products and char. A visible change in curves of FR-treated and FR cotton after Fenton's reaction can be seen as well, indicating the modification in cellulose matrix of all the samples. The FR-treated cotton showed a single prominent peak at 310 °C, whereas, the FR-treated cotton after the Fenton's reaction had a peak before 300 °C, exhibiting instability in FR treatment. The second peak of the FR-treated cotton after the Fenton's reaction fell in a similar temperature region as the untreated cotton sample. Moreover, the attributional area of the second peak was similar to that of the cotton, for instance cotton: after Fenton's reaction/1: 0.97. The ratio of decomposition peak in FR-treated cotton was lower than that of the cotton sample (cotton: FR-treated cotton/1: 0.49).

The thermal results from the DSC also indicated that the thermal decomposition for both samples of FR-treated cotton before and after Fenton's reaction were influenced by the organophosphorus compounds. The FR-treated cotton samples increased the char yields with the phosphates. The lowered decomposition temperature of FR-treated cotton in the presence of the organophosphorus flame retardant species showed its mode of action as a condensed phase flame retardant systems (Langley *et al.* 1980; Lam *et al.* 2011). By comparison, FR-treated cotton samples after Fenton's reaction, showed shift in the DSC curves, suggesting change in decomposition behavior of the FR-treated cotton.

From DSC the decomposition of a material can be assessed. The information provided by DSC is limited to the heat flow of sample degradation at high temperatures. To obtain the required information of heat generation by the combustion of the decomposition of products, testing methods such as TGA and DSC are generally insufficient to measure the pyrolysis and combustion characteristics (Yang *et al.* 2010, 2011). However, from the pyrolysis combustion flow calorimeter (PCFC) of the previous

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study, an increase of 51% was observed in total heat release (THR) [kJ/g] values during the combustion of FR cotton textiles after the degradation of flame retardant species from the fabric (Yasin *et al.* 2016a).

Gasification is considered to be a beneficial method to convert organic materials or biomass into the multipurpose gas known as syngas (synthesis gas). The energy valorization of non-conventional resources to save fossil fuels and reduce the generation of domestic and industrial waste has recently gained great attention. Accordingly, the waste is now transformed into valuable energy sources instead of being disposed. To have a better understanding of the gasification process, a customized spouted bed with unusual geometry (square based instead of circular) was developed for an easier scale-up (Fig. 1). The spouted bed gasifiers perform better in hydrodynamic control due to a low gas flow rate and a lower pressure drop (Massimo 2015). To understand the behavior, the hydrodynamic control of the density of prepared textile pellets was examined by feeding it to a granular bed made of a stationary inert phase, which acted as a thermal and hydrodynamic buffer (Massimo and Rovero 2015).
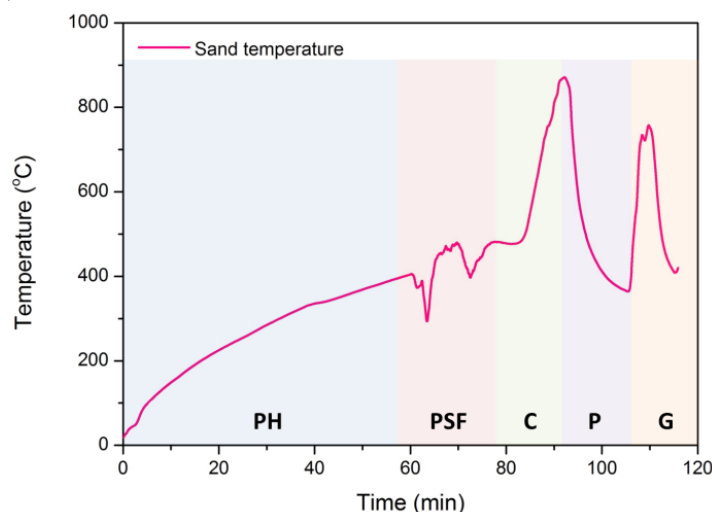

Fig. 7. Thermal transitory in the spouted bed gasifier with pre-heating (PH), pulsating solid feeding (PSF), combustion (C), pyrolysis (P), and gasification (G) regions

The rationale of preliminary experimentation is given by the order of different LPG/air (liquefied petroleum gas/air) ratios to establish feasible and easy reaction control over all possible operations (combustion, pyrolysis, or gasification). The initial step was the heating of the spouted bed to approximately 400 °C (by reading the thermocouple output in the sand bed); this temperature assured that the ignition point for the feed material had a standard composition. This step was performed by regulating the furnace thermal power at 11 kW with a suitable LPG flow rate and minimal extra-stoichiometric air. The desired temperature was reached in about 60 min, as shown in Fig. 7. A solid particulate combustion mode in the spouted bed was then chosen to speed up the reactor heating and reach the actual gasification temperature. The prompt peak of temperature at 90 min was given by the oxidative region. Subsequently, the air flow was decreased to have a reducing reaction mode (endothermic pyrolysis) in the interval between 90 min and 110 min. A partially oxidative region was used to gasify the pyrolytic solid residue previously generated, followed by the regulation of the LPG flow and the spraying of water in the pre-burner to maintain an adequate in-line steam generation (Massimo and Rovero 2015).
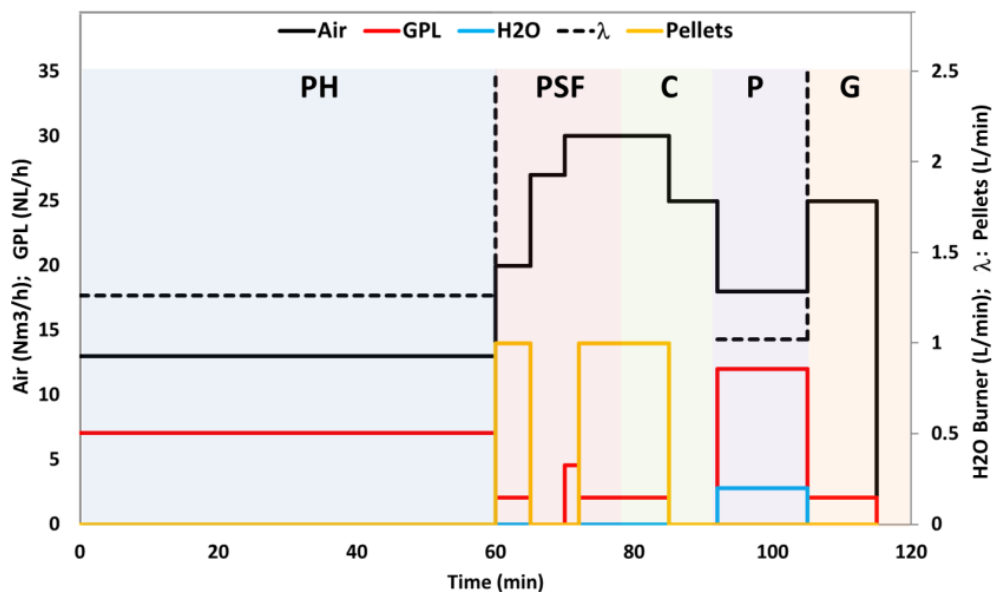
Fig. 8. Flow regulation in the spouted bed gasifier with pre-heating (PH), pulsating solid feeding (PSF), combustion (C), pyrolysis (P), and gasification (G) regions

The prepared textile pellets were transferred to the hopper of the gasification unit in order to attain a suitable feed rate. The feeding of textile pellets to the gasifier was maintained at the rate of 100 and 150 g/min. The gasification temperature reached > 700 °C with continuous feeding at 100 g/min; however the temperature was calculated higher around 900 ºC with increased feeding rate of 150 g/min. Figure 8 shows the different flow rates and thermal transitory in the variant conditions tested. The heating of the bed was initiated at approximately 400 °C for 60 min at 11 kW. At this pre-heating stage, a few wood pellets were added into the reactor, which helped in reducing the LPG flow rate and increased the air flow rate. This led to a high oxidized atmosphere ($\lambda \approx 1.20$) and total combustion of the feed material. Therefore, it provided an additional energy boost and for the enthalpy of the reaction to be transferred to the rig, which caused a sudden increase in temperature (Massimo 2015).

Higher temperatures lead to higher conversion efficiency, thus affecting the produced gas contents (hydrogen, carbon dioxide, carbon monoxide, and methane) that consequently increase the yield. Temperatures beyond 800 °C lead to steam formation and water-gas reactions due to the endothermic nature of the H_2 production reaction. This consequently increases the hydrogen content and decreases the methane content. Temperatures above 900 °C resulted in an increase of carbon monoxide and a decrease in tar content due to the reformation steam and the destruction of tar (Kumar *et al.* 2009). Consequently, an increment in the temperature increases the gas yield.

CONCLUSIONS

1. The thermogravimetric properties of the FR-treated cotton were destabilized after the degradation and elimination of permanent/durable FR product from the cotton fabric *via* an oxidation method (Fenton's reaction). The decomposition temperature of the FR-treated cotton after Fenton's reaction followed the similar curve path as of untreated cotton.

2. Considering the gasification temperature to be reached by the FR-treated cotton textiles at the custom-made gasifier, the preliminary results were carried out. The feeding rate of 150 g/min found to be optimum reaching the gasification temperature at 900 °C.

3. It is anticipated that the syngas produced from FR-treated cotton textiles after the degradation and elimination of FR substance will provide similar outcomes to those of untreated cotton textile.

ACKNOWLEDGMENTS

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